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## Process for the Conversion of Polysulfanes

### Field of the Invention

The invention relates to a process for the removal of polysulfanes from gas streams formed during  $H_2S$  synthesis.

### 5 Background

In  $H_2S$  syntheses from hydrogen and sulfur, polysulfanes ( $H_2S_n$ ) are generally found as by-products in the crude gas in an order of magnitude of  $\geq 400$  vpm (volume per million), and when the gas stream is compressed these tend  
10 to decompose in an uncontrolled manner into  $H_2S$  and sulfur. This leads to undesirable sulfur deposits in the whole of the compression area, including the peripheral pipes and valves.

It is known that polysulfanes are thermodynamically  
15 unstable and have a tendency to decompose, particularly when heated (M. Schmidt, W. Siebert: "Sulfane" in Comprehensive Inorganic Chemistry, vol. 2, sect. 2.1, Pergamon Press, Oxford 1973, 826-842).

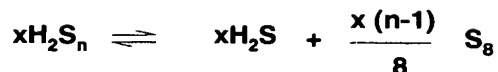
Traces of alkali on the surface of glass vessels lead to  
20 the deposition of elemental sulfur.

However, these findings come from investigations with polysulfanes present in more or less pure form.

In principle, of course, they also apply to polysulfanes present in great dilution.

25 In this case, however, the influence of the concentration ratios has to be taken into account.

Under the above circumstances, the polysulfanes are present in great dilution in hydrogen sulfide, which at the same time represents a decomposition product of the  
30 polysulfanes in a thermodynamic equilibrium:



The high  $\text{H}_2\text{S}$  concentration makes the shift of the equilibrium to the left-hand side seem probable and the decomposition of the polysulfanes into hydrogen sulfide and sulfur to be a non-preferred reaction.

The object of the invention is to provide a process for the practically complete removal of the polysulfanes, thus preventing sulfur deposits in the plant's pipes.

#### 10 Summary of the Invention

The invention provides a process for the removal of polysulfanes from crude gas formed during the production of hydrogen sulfide, characterized in that the crude gas, with a content of > 80 vol., preferably > 95 vol.  $\text{H}_2\text{S}$  and > 100 to 2000 vpm, particularly > 400 to 1500 vpm, of polysulfanes ( $\text{H}_2\text{S}_n$  with  $n$ : 2 to 8), is passed through an optionally multi-stage washer system, brought into contact with water and/or methanol, preferably with basic aqueous and/or methanol systems, and a pure gas is obtained in which the polysulfanes are present depleted by > 50 to > 99.5%, based on the starting value.

The quantities of polysulfanes can optionally also be more than 2000 vpm.

#### Detailed Description of the Invention

25 Jet washers are preferably used, which, like other washers, can be operated at a pressure of 1.05 to 10 bara, preferably at 1.05 to 2 bara.

Unpressurized operation is an alternative, however. In particular, aqueous and/or methanolic 0.5 to 20 wt.%, preferably 0.5 to 10 wt.%, solutions of alkali hydroxides

or oxides, especially KOH/KHS or NaOH/NaHS solutions, are used as washing fluid.

The hydrogen sulfides are formed while passing the gas streams through the washing fluid.

- 5 Appropriately concentrated solutions of other basic oxides or hydroxides, especially of alkaline earth hydroxides or oxides, preferably those of calcium, can also be used.

The polysulfanes are also removed from the gas streams by basic aqueous and/or methanolic 1 - 20%, preferably 1 to 10 wt.%, solutions of ammonia, organic amines, of the general formula  $(C_nH_{2n+1})_xNH_y$  with  $n=1, 2, 3$ ;  $x = 2, 3$ ;  $y=0, 1$  or amino alcohols of the general formula  $(C_nH_{2n+1}O)_xNH_y$  with  $n=1, 2, 3$ ;  $x=2, 3$ ;  $y=0, 1$ .

The suitable temperature range is generally between 0 and 15 150°C, especially 10 and 60°C.

At gas velocities of the crude gas to be purified of generally between 0.1 and 25 m/s, especially 10 and 22 m/s, the polysulfanes are removed from the gas streams with a degree of depletion of > 50 to > 99.5%, preferably 20 > 70 to > 99.5%, based on the starting content in the crude gas.

For a content of > 500 vpm in the crude gas, this corresponds to a depletion to < 10 vpm in the pure gas.

The sulfur formed during the conversion of the polysulfanes goes into solution, among other things as a 25 result of the formation of the corresponding polysulfides. Sulfur precipitated in solid form can optionally be discharged with the aid of suitable filtration devices. The washing solution circulates and is discharged as a 30 function of the polysulfide/sulfur load. The washing fluid is topped up as a function of the rate of discharge and of quantities of solvent that may evaporate. To remove any

residual quantities of polysulfanes present after the jet washer (generally  $\leq 20\%$  of the starting quantity), the  $H_2S$ -containing gas is generally after-treated with the above-mentioned solutions in a washing column or a packed  
5 bed in counter-current (counter-current washer). Entrained droplets are separated by means of a demister system. Any quantities of sulfane remaining in the gas stream of purified  $H_2S$  can also be broken down in a downstream adsorber bed (activated carbon, zeolite) and the sulfur  
10 formed can be separated off.

#### Analytical

The analytical acquisition of the sulfane concentration in the crude and pure gas takes place by means of an online UV measurement. Parallel to this, sulfur contents in the  
15 washing solution and sulfane and sulfur concentration in the  $H_2S$ -containing gas stream are determined by wet-chemical means as required.

With the aid of the process according to the invention, it is possible to deplete the polysulfanes to such an extent  
20 that, in downstream processes, e.g. compressor stages, undesirable sulfur deposits are avoided..

#### Examples

Crude gases with a polysulfane content of  $> 400$  to 2000 vpm are used.

25 The polysulfane concentrations are dependent upon the reaction conditions in the  $H_2S$  reactor.

#### Comparative Example 1

$H_2S$  crude gas was passed through an adsorption column packed with approx. 7 l of etched Raschig rings at  
30 20  $Nm^3/h$ . The sulfur forming by decomposition of the polysulfanes was deposited on the surface of the packings.

A degree of depletion of 25% was achieved. Service life of the adsorber bed 20 h.

Comparative Example 2

H<sub>2</sub>S crude gas was passed through an adsorption column  
5 packed with approx. 7 l of SiO<sub>2</sub> supports (particle size 3  
- 5 mm) at 20 Nm<sup>3</sup>/h. The sulfur forming by decomposition  
of the polysulfanes was deposited on the surface of the  
packings. A degree of depletion of 50% was achieved.  
Service life of the adsorber bed 48 h.

10 Example 1

H<sub>2</sub>S crude gas was passed first through a jet washer system  
operated only with water and then through an adsorption  
column packed with approx. 12 l of activated carbon  
(particle size 5 - 6 mm) at 200 Nm<sup>3</sup>/h for 60 h. Before  
15 entering the adsorption column, a degree of depletion of  
75% and after the column a value of > 99% was measured.

Example 2

H<sub>2</sub>S crude gas was passed first through a jet washer system  
supplied with methanol at 200 Nm<sup>3</sup>/h for 48 h. A degree of  
20 depletion of > 50% was achieved, based on the crude gas.

Example 3

H<sub>2</sub>S crude gas was passed first through a washing column  
operated with a methanol/triethanolamine mixture (5%  
triethanolamine) for 24 h at 10 Nm<sup>3</sup>/h. The sulfur forming  
25 as a result of decomposition of polysulfanes dissolved in  
the washing solution. A degree of depletion of 80% was  
achieved.

Example 4

H<sub>2</sub>S crude gas was passed through a jet washer system supplied with a methanol/NaOH mixture (5% NaOH) for 400 h at 200 Nm<sup>3</sup>/h. A degree of depletion of 99% was achieved.

The sulfur deposited after a running time of approx. 200 h  
5 was removed from the washer circulation with the aid of in-line filtration.

#### Example 5

H<sub>2</sub>S crude gas was passed through a jet washer system supplied with a water/KOH mixture (12% KOH) for 200 h at  
10 200 Nm<sup>3</sup>/h. A degree of depletion of 99.5% was achieved.